November 15, 1996

MEMORANDUM

TO: Orville D. Green, Assistant Administrator
Air & Hazardous Waste

FROM: Martin Bauer, Chief
Air Quality Permitting Bureau

SUBJECT: Issuance of Tier II Operating Permit #083-00063
Northwest Foam Products, Incorporated; Twin Falls

PURPOSE

The purpose of this memorandum is to satisfy the requirements of IDAPA 16.01.01 Sections 400 through 406 (Rules for the Control of Air Pollution in Idaho) for issuing Operating Permits.

FACILITY DESCRIPTION

Northwest Foam Products (Northwest Foam) produces expanded polystyrene (EPS) bead products such as block foam insulation, packaging materials, and architectural materials. The processes utilized in the production of these foam products include bead pre-expansion, drying, prepuff aging, block molding, aging, and product aging. Emissions from the production of EPS products are primarily volatile organic compounds (VOCs)

PROJECT DESCRIPTION

This project involves the issuance of a Tier II Operating Permit (OP) that limits the potential to emit of volatile organic compounds (VOCs) from Northwest Foam Product's Twin Falls, Idaho, facility.

SUMMARY OF EVENTS

DEQ received Northwest Foam's Tier II OP application on December 22, 1995. On June 30, 1996, DEQ deemed Northwest Foam's application complete.

On September 17, 1996, a proposed Tier II permit was issued for public comment. The public comment period was from October 1, 1996, through October 31, 1996. No comments were received.

RECOMMENDATIONS

Based on the review of the Tier II OP application materials and of applicable state and federal rules and regulations concerning the permitting of air pollution sources, the Bureau recommends Northwest Foam Products, Inc., Twin Falls, be issued a Tier II OP. Staff members also recommend that the facility be notified in writing of the obligation to pay permit application fees for the Tier II OP.

MB\SJR\ABC:jrj...\permit\nwfoam/nwfoamf.IMM

Attachment

cc: D. Howard, Twin Falls Regional Office
Source File
COF

August 30, 1996

MEMORANDUM

TO: Martin Bauer, Chief
Air Quality Permitting Bureau
Air & Hazardous Waste

FROM: Almer B. Casile, Air Quality Engineer
Air Quality Permitting Bureau
Operating Permits

THROUGH: Susan J. Richards, Air Quality Permits Manager
Air Quality Permitting Bureau
Operating Permits

SUBJECT: Technical Analysis for Proposed Tier II Operating Permit #083-00063
Northwest Foam Products, Incorporated; Twin Falls

PURPOSE

The purpose of this memorandum is to satisfy the requirements of IDAPA 16.01.01 Sections 400 through 406 (Rules for the Control of Air Pollution in Idaho) for issuing Operating Permits.

FACILITY DESCRIPTION

Northwest Foam Products (Northwest Foam) produces expanded polystyrene (EPS) bead products such as block foam insulation, packaging materials, and architectural materials. The processes utilized in the production of these foam products include bead pre-expansion, drying, prepuff aging, block molding, aging, and product aging. Emissions from the production of EPS products are primarily volatile organic compounds (VOCs). Please note that for this Permit the raw beads are considered the emission unit.

PROJECT DESCRIPTION

This project involves the issuance of a Tier II Operating Permit (OP) that limits the potential to emit of volatile organic compounds (VOCs) from Northwest Foam's Twin Falls, Idaho, facility.

SUMMARY OF EVENTS

DEQ received Northwest Foam's Tier II OP application on December 22, 1995, and deemed the application incomplete on January 19, 1996. On February 26, 1996, DEQ received Northwest Foam's February 22, 1996, request for an extension to respond to DEQ's incompleteness letter. On February 27, 1996, DEQ received Northwest Foam's response to DEQ's incompleteness letter. DEQ determined the response to be incomplete on March 27, 1996. On April 17, 1996, Northwest Foam faxed DEQ an analysis of actual and potential emissions in order to prove that Northwest Foam was not a major facility. Also on that day, John M°Creedy of Jim Jones & Associates, representing Northwest Foam, requested a copy of the calculations DEQ used to determine that Northwest Foam was a major facility. On April 18, 1996, DEQ officials met with Northwest Foam and its attorney to discuss registration fees and permitting issues. On April 22, 1996, DEQ sent Northwest Foam a letter of notice stating that their application was incomplete, and that a Tier I OP may be due.

On May 1, 1996, DEQ received Northwest Foam's April 30, 1996, response to one of the items on the DEQ's March 27, 1996, incompleteness letter. On May 2, 1996, the Office of the Attorney General sent Northwest Foam a cover letter and consent order for signature. The cover letter also requested information regarding an equation referenced in Northwest Foam's letter dated April 30, 1996. On May 16, 1996, DEQ received the requested information from the Office of the Attorney General. On May 23, 1996, DEQ requested that Northwest Foam submit requested short- and long-term emissions and the accompanying compliance procedures needed to assure compliance with the requested emission limits. On May 31, 1996, DEQ received the requested information. On June 30, 1996, DEQ deemed Northwest Foam's application complete.

DISCUSSION

1.   Area Classification

       The facility is located in Twin Falls, Idaho, which is classified as attainment or unclassifiable for all criteria pollutants.

2.   Emission Estimates

An emission estimate for the facility was performed on the boiler and EPS manufacturing process. Estimates were performed only for volatile organic compounds (VOCs) because the facility is major only for VOCs. Initial estimates for the 5.021 million BTU per hour boiler (see Appendix A) showed that annual VOC emissions were negligible (i.e., less than 2 tons). Estimates of VOC emissions from the manufacturing process are given in Appendix A. Please note that this VOC analysis is based on the pentane content of the raw bead. Pentane is the blowing agent currently used in the raw bead. No emission estimates were performed for a blowing agent considered as a toxic air pollutant (TAP). The introduction of a TAP blowing agent, or blowing agent partially made up of a TAP could be considered a modification under Section 200 of the Rules.

Originally, DEQ had concerns that Northwest Foam was major for methylene diphenyl diisocyanate (MDI). However, a review of calculations and supporting information submitted by Northwest Foam demonstrated that the facility was minor for MDI. The calculations submitted by the facility vary somewhat from the equations given in the Robert W. Powell documentation that was submitted to DEQ. The differences in the values are significant. However, the final numbers for both equations are well below the major facility applicability threshold. These calculations can be found in Appendix A.

VOC emission rate limits in the Permit are based on the assumptions that the average pentane (i.e., VOC) content, in percent by weight, left in the molded product after 48 hours is 15% of the original content and that the pentane content in the EPS beads would be the value given in the bead supplier's certificate of analysis (CA). The 15% retention was taken from the OAQPS document *Control of VOC Emissions From Polystyrene Foam Manufacturing* submitted as part of the application. It was also assumed that the percent by weight VOC content would not vary after 48 hrs. All calculations were based on these assumptions. Please note those EPS beads used in the process are considered the emission units in this process. This assumption was made because emissions are from the beads and not the process equipment.

Northwest requested a short-term emission rate limit of 13 tons VOC per month, and a long-term emission rate limit of 90 tons VOC per 12 month period. Based on the 15% retention mentioned above, short- and long-term operating requirements were determined. These requirements were determined as follows:

Determination of Operating Requirement

From Northwest Foam's May 30, 1996, request to limit their potential to emit of VOCs to 90 tons per year and given the 15% retention mentioned above, a total VOC content (105.9 tons per year) in the annual and monthly amount, respectively, of EPS beads was determined. The value, the operating requirement (OR), was determined as follows:

OR   = ERL * (1-0.15)
                                = 105.9 tons per year
                                = 15.3 tons per month

where,   OR   =   total VOC content in the annual and monthly amount of EPS beads used
                                ERL =   requested annual emission rate limit (90 tons VOC per year, 13 tons VOC per month
                                (1-0.15)= decimal percent of VOC in beads released to the atmosphere

Based on pentane content given in the CA, compliance with the short- and long-term operating requirements can be determined as follows:

VOC$_{each}$ =   M$_{EPS}$ * %VOC$_{EPS}$, where

VOC$_{each}$ =   pounds (lbs.) of VOC contained in the pounds of EPS used;
M$_{EPS}$ =   pounds (lbs.) of EPS used;
%VOC$_{EPS}$ =   weight percent given by CA of the supplier of the given bead,

        and

$$VOC_{month} = \sum(VOC_{each}) = VOC_{each} + VOC_{each} + \ldots \text{ where,}$$

$$\sum(VOC_{each}) = \text{total pounds of VOC contained in the pounds of EPS used for each shift (lbs. VOC/shift) of the month}$$

$$VOC_{12} = \sum VOC_{month} = VOC_{month} + VOC_{month} + \ldots \text{ where,}$$

$$VOC_{12} = \text{sum of } VOC_{month} \text{ for the most recent 12 month period}$$

The operating requirements given in Section 2 of the OP have been included as a surrogate to compliance with the emission rate limit. In actuality, the operating requirement only limits the total VOC content in the EPS beads used by the facility. To determine the estimate emission rate the following calculation must be performed.

$$\text{VOC Emissions} = VOC * (1-0.15)$$

where, VOC = represents either VOC_{month} or VOC_{12},

$(1-0.15)$ = % VOC released to the atmosphere after 48 hours

VOC Emissions = represents either monthly or annual emissions, depending what VOC value was used

This calculation was not included in the Permit because the procedure can easily be performed by DEQ. Compliance with the operating requirements provides more than adequate assurance with emission rate limits in the permit as long as all of the monitoring and record keeping requirements are fulfilled.

3.   Facility Classification

Without federally enforceable permit conditions, this facility would be considered major for VOCs, as defined in IDAPA 16.01.01.006.54. The facility is no longer considered major, however, because the proposed permit limits the facility's potential to emit below 100 T/yr for VOCs. The facility is not a designated facility, as defined in IDAPA 16.01.01.006.25. facility (SIC 3674).

4.   Regulatory Review

This OP is subject to the following permitting regulations:

IDAPA 16.01.01.006	Definitions;
IDAPA 16.01.01.401	Tier II Operating Permit;
IDAPA 16.01.01.402	Application Procedures;
IDAPA 16.01.01.403	Permit Requirements;
IDAPA 16.01.01.404	Procedure for Issuing Permits;
IDAPA 16.01.01.405	Conditions for Tier II Operating Permit;
IDAPA 16.01.01.406	Obligation to Comply;
IDAPA 16.01.01.470	Permit Application Fees for Tier II Permits;
IDAPA 16.01.01.625	Visible Emissions Limitations;

The boilers were analyzed to determine if they are subject to 40 CAR 60.40C, Standards of Performance for Small Industrial-Commercial-Institutional Steam-Generating Units. In order for the boilers to be affected, they must have a capacity greater than ten (10) MMBtu/hr. Since the capacity of the boilers is only 5.37 MMBtu/hr, they are not subject to the NSPS requirements.

AIRS

The abbreviated AIRS data entry sheet is located in Appendix B.

FEES

This facility is not a major facility as defined in IDAPA 16.01.01.008.14. Therefore, registration and registration fees, in accordance with IDAPA 16.01.01.526 are not applicable. Permit application fees, in accordance with IDAPA 16.01.01.470, are, however, applicable.

RECOMMENDATIONS

Based on the review of the Tier II OP application materials and of applicable state and federal rules and regulations concerning the permitting of air pollution sources, the Bureau staff recommends Northwest Foam Products, Incorporated, Twin Falls, be issued a proposed Tier II OP. An opportunity for public comment on the air quality aspects of the proposed permit shall be provided as required by IDAPA 16.01.01.404.01. Staff also recommends that the facility be notified in writing of the obligation to pay permit application fees for the Tier II OP.

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Attachment

cc: R. Lupton, SCIRO
        Source File
        COF

APPENDIX A

Facility Name: Northwest Foam Products, Incorporated
Address: 2390 Rostron Circle
City, State, Zip: Twin Falls, Idaho 83301
DEQ Project Engineer: Almer B. Casile

Determination of Operating Requirement

From NW Foam's May 30 request to limit their potential to emit to 90 tons per year and given the 15% retention given from previous submittal, a total VOC content (105.9 tons per year) in the annual amount of EPS beads was determined. The value was determined as follows:

$$\sum (VOC_{each}),$$

$$= 90 \text{ tons VOC per year} * (1-0.15)$$
$$= 105.9 \text{ tons per year}$$

$$= 13 \text{ tons VOC per month} * (1-0.15)$$
$$= 15.3 \text{ tons per month}$$

where,

$\sum (VOC_{each})$ = total VOC content in the monthly/annual amount of EPS beads used
90 tons per year = requested annual emission rate limit
13 tons per month = requested monthly emission rate limit
(1-0.15) = decimal percent of VOC in beads release to the atmosphere

VOC_{each} equals $\sum (VOC_{each}$.

M_{EPS} = pounds (lbs) of EPS used;
$\%VOC_{EPS}$ = highest percent by weight VOC content given in the Certificate of Analysis for the EPS bead used,

0.10 = % VOC content in EPS beads (assumed worst case)

NO$_x$ Estimates for the 5.021 million Btu per Hour Boiler

$5.021*10^6$ Btu per hour * 100 lbs NO$_x$ per 10^6 ft^3 naturals gas ÷ 950 Btu per ft^3 * 8760 hours per year

$$= 4630 \text{ lbs NO}_x \text{ per year}$$
$$= 2.31 \text{ tons NO}_x \text{ per year}$$

VOC Estimates for the 5.021 million Btu per Hour Boiler

Replacing the emission factor for NO$_x$ with the VOC emission factor of 8 lbs VOC per 10^6 ft^3 naturals gas yields the following values:

$$370 \text{ lbs VOC per year}$$
$$0.18 \text{ tons VOC per year}$$

Comparison of MDI Emissions Calculations

Equation from the article *Estimating Worker Exposure to Gases and Vapors and Leaking from Pumps and Valves, Robert W. Powell*:

$$W = 79.6 \cdot \left(\frac{P^{\circ}_T M_T}{T} \right) \cdot u^{0.78} \cdot r^{1.89} = 79.6 \left(\frac{7.89 \cdot 10^{-6} \cdot 250}{294.15\,^{\circ}K} \right) \cdot 3^{0.78} \cdot 20.40^{1.89} = 0.375 \; g/s$$

where

M_T	$=$	material average molecular weight, g/g mol (250 g/g mol for MDI)
P°_T	$=$	liquid vapor pressure in atmospheres, atm
T	$=$	temperature in °Kelvin, °K
u	$=$	wind speed in meter per second, m/s
r	$=$	radius of spilled liquid material in meters, m
	$=$	as given in by J. McCreedy on April 30 on behalf of NW Foam, total surface area cover in 1995 was 1,308 m². The equivalent radius for this surface area is

$$r = \sqrt{\frac{Area}{\Pi}} = \sqrt{\frac{1308 \; m^2}{\Pi}} = 20.40 \; m$$

W	$=$	evaporation rate in grams per second, g/s

When this value is multiplied by the longest time the blocks are aged (6 weeks), the annual emission rate of MDI can be determined. Hourly emission rate can be determined by multiplying by the number of seconds per hour, 3600 sec.

The calculations are as follows:

$$Annual \; Emission \; Rate, \; tons \; per \; year = \frac{0.376 \; grams}{sec} \cdot \frac{6 weeks}{year} \cdot \frac{7 days}{1 \; week} \cdot \frac{86,400 seconds}{1 \; day} \cdot \frac{1 \; lb}{453.59 grams} \cdot \frac{1 ton}{2000 lbs}$$

which equals 1.50 tons MDI per year

Estimating Worker Exposure to Gases and Vapors Leaking from Pumps and Valves

ROBERT W. POWELL

Exxon Research and Engineering Company, Florham Park, NJ 07932

The industrial hygienist is frequently asked by a process design group about the required level of engineering control for toxic materials in process streams. The potential hazard to the worker is not only a function of the toxic material concentration in the process stream, but also the equipment (point source) characteristics and the process stream properties. Not all of these parameters can be evaluated for streams and complex processes still on the drawing board. However, the hygienist can estimate worker exposure due to potential leaks or spills from equipment. This paper presents a method that can be used to estimate the concentration of a toxic material in a worker's breathing zone, based upon the concentration of the material in the process stream, the process stream properties, and the equipment leak potential. The paper concentrates on leaks from pumps and valves, but the method is applicable to leaks from other types of process equipment. The method is a three step process consisting of estimating the equipment leak potential, calculating the amount of a vaporized leaking contaminant, and estimating the concentration of gas or vapor at the worker's nose via a dispersion calculation. For material evaporating from out-of-service equipment, the calculation method combines an evaporation model with a dispersion model to estimate the concentration of contaminant in the worker's breathing zone. Once a worker exposure estimate exists, the industrial hygienist can determine the type of engineering control required for the equipment.

Introduction

More and more frequently the industrial hygienist, environmental engineer takes part in the engineering design review process. During these reviews, industrial hygienists and design engineers consult on questions of material toxicity, worker exposure, and engineering control. Everyone's goal is a productive plant that will not overexpose workers to toxic materials and will avoid expensive and time-consuming retrofits.

During the design review, discussions center on locations in the design where toxic materials may evolve from process streams, e.g., pump seals, valve stems, sample points, etc. A designer may ask, "If I have X% hydrogen sulfide in this pump, do I need a single or a double mechanical seal?" The industrial hygienist needs more than the toxic material concentration and a Threshold Limit Value to answer this question. He needs an estimate of leakage and the potential concentration of toxic materials that will occur in the worker's breathing zone to compare with the TLV. The pump location, size, service, leak potential, etc., and the material solubility, vapor pressure, toxicity, dispersion characteristics, etc. are parameters that assist the decision-making process. However, not all of these parameters can be evaluated for complex processes and streams in designs still on the drawing board. Estimates of these parameters are necessary.

The industrial hygienist often relies on exposure data from similar equipment and process streams to decide if a proposed engineering control is adequate. Although some emission data are available,[1] exposure data from specific sources are almost non-existent. Therefore, the industrial hygienist must estimate worker exposure based on the equipment and stream information available.

One major part of an exposure estimation method is a dispersion model. Gaussian dispersion models[2] estimate the maximum ground level concentration of a contaminant issuing from a stack. In combination with Pasquill-Gifford dispersion coefficients, a Gaussian model can fairly accurately predict downwind concentrations. However, concentration estimates for distances less than 50 meters are not yet verified. Jet expansion equations have been used to estimate the concentration of H_2S at points up to 50 meters from a high pressure leak.[3] However, these equations are applicable only for valves or flanges that have catastrophically failed and emit vapor at a velocity that is not described by an eddy diffusion equation (Pasquill-Gifford). Catastrophic equipment failures are normally corrected immediately, and hence are not usually long-term sources of worker exposure.

Before a dispersion model can be used to predict worker exposures, the amount of contaminant leaking into the atmosphere must be estimated. This emission rate varies with the type of equipment, the equipment maintenance history, auxiliary engineering controls, etc. A major report on emissions from refinery equipment is the Radian study conducted for the U.S. Environmental Protection Agency.[4] Radian sampled 500-600 sources in 14 refineries and determined average emission rates for flanges, compressors, valves, pumps, and drains. Data from the Radian study and similar studies[5] are usually collected by bagging leaking equipment and measuring the amount of collected gases and vapors. Unfortunately, the studies did not measure the amount of liquid leakage, which can be directly related to the quality of the valve packing or pump seal. Also, since the data were collected for air pollution purposes, the average leak rates are statistically emphasized while information on maximum rates (of importance to the industrial hygienist) is incomplete.

Emission data are normally collected during equipment operation when the sealing mechanisms are assembled. Dur-

ing maintenance, when equipment is not in service and a pump or valve is disassembled, residual material can evaporate and disperse to the worker's breathing zone. Evaporation models are available[6] that, based on the properties of the material, estimate the rate of material evaporation.

After the worker exposure concentration is estimated for a potential leak, the industrial hygienist must decide if the equipment requires additional engineering controls. Usually he compares the exposure concentration with the TLV-TWA (Threshold Limit Value - Time Weighted Average) and/or the TLV-STEL (Short-Term Exposure Limit).[7]

This paper describes methods of estimating the concentration of a toxic material in a worker's breathing zone caused by leaking process equipment, particularly pumps. Given the concentration of a toxic material in a process stream, the process stream properties, and an estimate of the leak potential of the equipment, these methods can be used to calculate the fraction of material vaporized from liquids and the vapor or gas concentration at a worker location. After a description of the estimation methods, examples are presented for pumps and valves, the two types of refinery equipment most likely to leak according to the Radian survey.

If the liquid leak rate is known or estimated, the method described in this paper calculates the amount of vaporized liquid and the concentration of contaminant in the vapor, and estimates the dispersion concentration of contaminant downwind of the leak. If the vapor emission rate is known or estimated, the method calculates the concentration of contaminant in the vapor, and then estimates the vapor dispersion. For out-of-service equipment, the method first estimates the evaporation rate of the material, then the dispersion of the vapor.

Operating Pump and Valve Leakage

Figure 1 shows a centrifugal pump single mechanical seal with a back-up throttle bushing. The area to the left (inside) of the seal is called the stuffingbox or inner seal cavity. The area to the right (outside) of the seal is called the outer seal cavity. Spring force and the hydraulic force due to the pressure of the pumped fluid push the rotating seal ring against the stationary seal ring thereby preventing significant leakage past the seal surfaces. American Petroleum Institute Standard 610[8] requires that a throttle bushing be installed outside the seal to help contain material that leaks past the seal. Many nonpetroleum pumps do not have this throttle bushing, and hence material that leaks past the mechanical seal is released directly to the atmosphere.

If a single mechanical seal with a throttle bushing fails catastrophically, pumped fluid spurts past the seal, through the clearance between the shaft sleeve and the throttle bushing, and sprays into the atmosphere. To reduce the amount of leakage to the atmosphere, an auxiliary ring of Grafoil packing or equivalent (Figure 2), instead of a throttle bushing, can be installed behind the seal. Since a smaller clearance is possible with the Grafoil packing compared to the throttle bushing, the packing retains more of the leaking material within the pump outer seal cavity, and the liquid flows through the quench drain.

Under normal conditions, the leak rate through mechanical seal faces is less than 5 mL (milliliters) per hour. However, pump seals can fail gradually accompanied by increasing leak rates. Eventually, the seal faces may wear unevenly and permit liquid leak rates through the seal to reach 40 liters per hour. Most of this liquid flows into the quench drain. But volatile material can flash in the outer seal cavity and
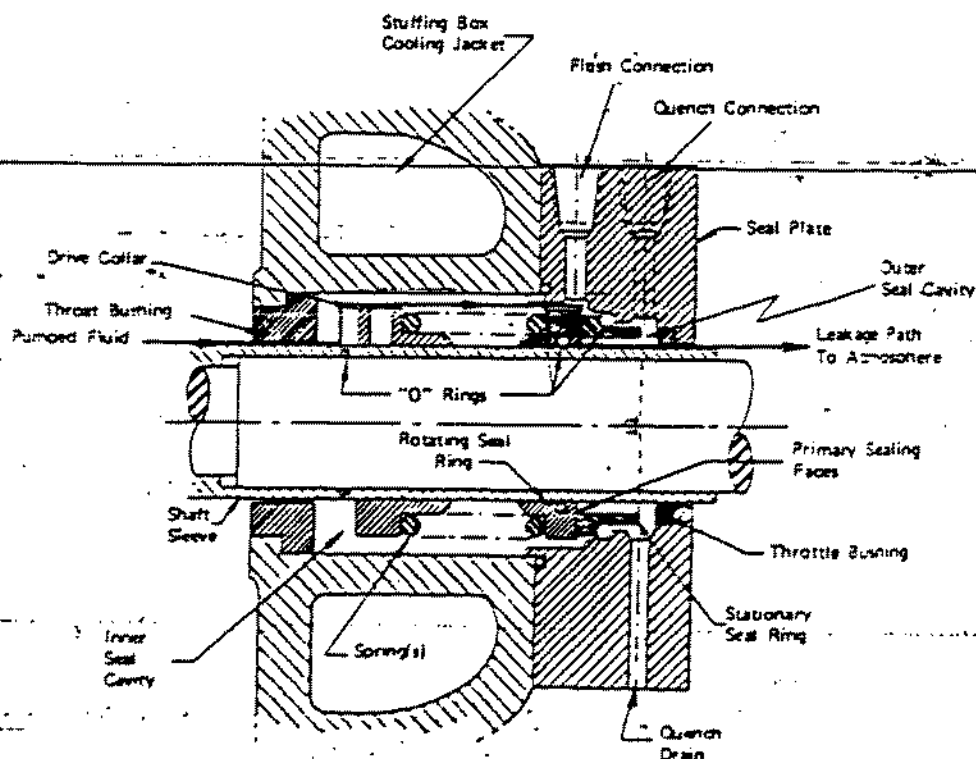

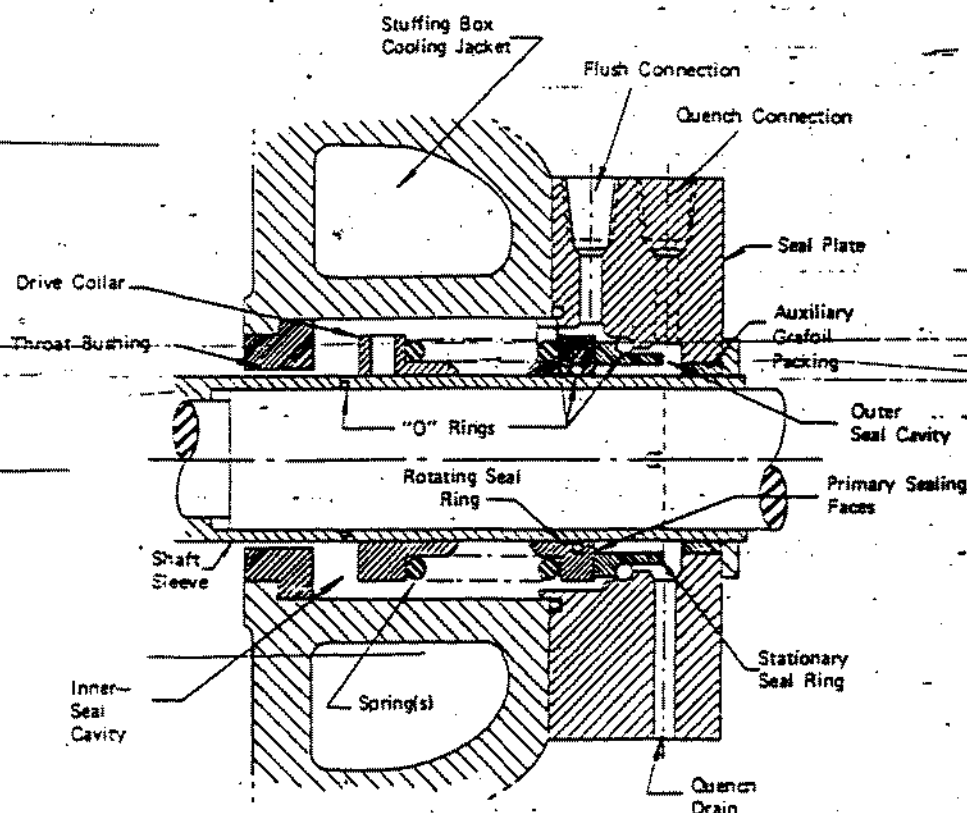Figure 1 — Centrifugal pump single mechanical seal

Figure 2 — Centrifugal pump single mechanical seal with auxiliary Grafoil packing.

escape to the atmosphere through the gap between the throttle bushing or auxiliary packing and the shaft sleeve.

The pump leak rate of importance from a worker exposure standpoint is the maximum rate tolerated by the operator before the pump is shut down for maintenance. This rate varies from plant-to-plant, operator-to-operator, and stream-to-stream. If the pump seal leak is pouring out several liters of liquid per minute onto the pump pad or surrounding area, the pump will be immediately shut down (particularly if a spare is available). In the event a spare pump is unavailable and the pump service is critical, the operator may allow the pump to continue to run with a severely leaking seal. Moreover, if the pump drains are closed and liquid leakage is not visible, the leak rate could be as high as 60 liters per minute. This, of course, is an extreme.

Unfortunately, the studies referenced in this paper do not contain estimates of liquid leak rates. Also, plant operators normally do not measure a leak rate when a seal leak problem exists. As an example, an unpublished survey concluded that an estimated leak rate of 7.6 liters (2 gallons) per hour was not of sufficient severity or concern to require shutdown of a pump for maintenance. Before the exposure estimation method is used, the designer and industrial hygienist should choose a realistic maximum pump leak rate based on general plant and company experience. This estimate of liquid leak rate past the seal can be used to obtain a vapor emission rate.

Emission data normally reported are almost always vapor leak rates, not liquid leak rates. Therefore, maximum vapor leak rates will probably have to be used in the estimation

method in the absence of liquid leak rate data. Estimates of average volatile emission rates from intact single pump seals have ranged from 6.8-114 grams (0.015-0.25 pounds) per hour.[9] However, the maximum-tolerable leak rate, which is the emission rate most likely to overexpose a worker, is normally not defined in the literature. The Radian report estimates 0.341 g/s (2.7 pounds per hour) as a vapor leak rate for the worst 5 percent of the leaking pumps in light liquid service. The designer-industrial hygienist team must decide if more accurate liquid leak rate estimates are available. For example purposes, a vapor leak rate of 0.341 g/s has been chosen for pumps in hydrocarbon service as a worst-case pump leak rate.

For valves (see Figure 3), there is no estimate of liquid leak rate. A liquid leak is usually visible and the leaking valve is quickly removed from service or the packing is adjusted to minimize the leak. The Radian report tabulates vapor leak rates for valves in light and heavy liquid service, gas/vapor streams, and hydrogen service. The leak rate cited for the worst 5 percent of values in light liquid service is 0.038 gm/s (0.3 pounds per hour) of vapor. This value is used in an example presented later in this paper.

Contaminant Vaporization from Operating Equipment

When a liquid contaminant leaks past a single mechanical pump seal, the contaminant vaporized in the pump seal cavity will discharge to the atmosphere, and may cause a worker exposure problem. Mists or aerosols may be an additional problem, but auxiliary Grafoil packing or even a
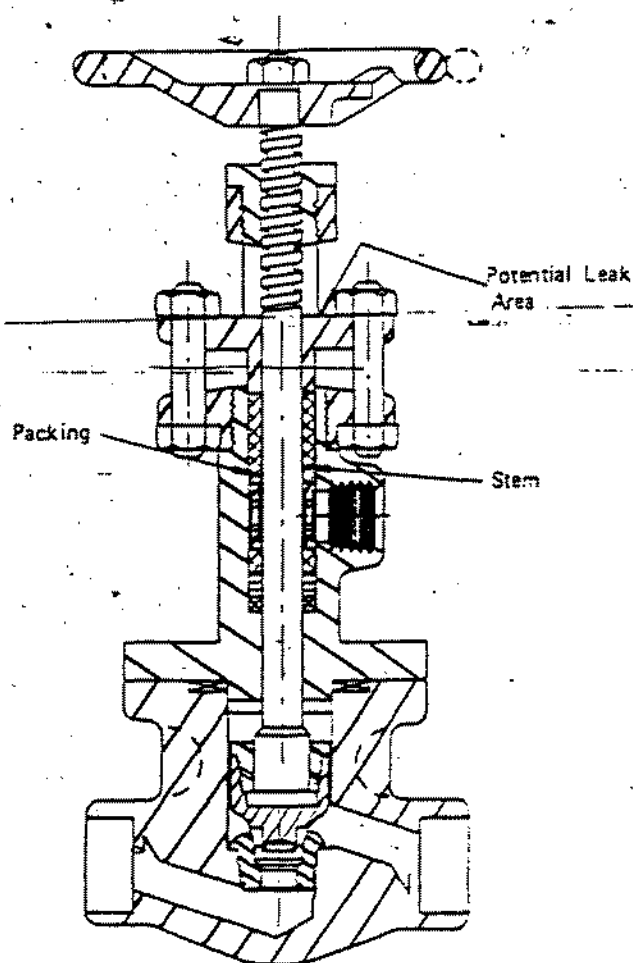
Figure 3 — Cross section of a typical globe valve.

well-maintained throttle bushing should minimize mist emissions. Whether or not a vapor condenses to an aerosol between the pump and the worker's nose is not important in the calculations in this article.

In petroleum refinery process streams there are two major types of contaminants in liquid streams: (1) gases in solution, e.g., H_2S in water or hydrocarbon; and (2) light components in hydrocarbon mixtures. A calculation to determine the amount of contaminant vaporized from an aqueous or hydrocarbon stream is shown in Table 1.

For gases in solution where the liquid leak rate is known or estimated:

$$Q = (C - C_a) L \qquad (1)$$

(see Table 1 for definitions).

Assuming that the liquid does not flash, the amount of gas contaminant that vaporizes from the solution as the liquid leaks through the pump seal is the difference between the amount in the process stream and the amount that remains dissolved in the liquid. The concentration of gas remaining in the liquid is a function of temperature and the other components in the stream. A well-buffered, caustic solution, such as a monoethanolamine solution, holds more H_2S in solution

than a neutral pH water. For most high-strength, refinery waters containing over 2 weight percent H_2S, the H_2S remaining in the water after vaporization (C_a) is negligible compared to the concentration prior to vaporization (C). As an example, the maximum amount of H_2S dissolved in water at 303 K is 0.26 weight percent at atmospheric pressure.

For liquid hydrocarbon mixtures leaking through pump seals, calculating the amount and type of vaporized contaminants is more difficult than calculating the amount of gas emanating from a solvent. If the mixture is pumped at a temperature above its bubble point, some material will flash as it crosses the seal faces, generating a large vapor release from the seal cavity due to the pressure increase. Alternatively, if the liquid in the pump is below its bubble point, there will be mixture of vapor and liquid in the pump seal cavity due to the seal leak. For this latter case, an equilibrium will be established between the two phases in the cavity. In this equilibrium condition, diffusion is the driving force for vapor leakage past the auxiliary pump packing, and consequently vapor leakage is negligible compared to the vapor leakage when the leaking liquid is flashing.

Calculations of vapor emission rates for hydrocarbon mixtures above their bubble points leaking through a seal are based on the assumption that the operation is an adiabatic flash vaporization. Although seal friction forces add heat to the fluid under normal sealing conditions, seal faces leaking at rates potentially harmful to workers are separated sufficiently by the leaking liquid so that heat input to the fluid is not significant.[?]

The following basic equations for a flash vaporization calculation are a mass balance and an enthalpy balance:

$$L = V - W \qquad (2)$$

$$Lh_l = Vh_v - Wh_w \qquad (3)$$

where   L = liquid leak rate (g mol/s)

V = vapor rate from flashed material (g mol/s)

W = liquid rate from flashed material (g mol/s)

h_l = enthalpy of stream L (kJ/g mol)

h_v = enthalpy of stream V (kJ/g mol)

h_w = enthalpy of stream W (kJ/g mol)

After V and W are calculated (via trial-and-error at different temperatures), the following equations for each component give the amount of contaminant in the vapor (y):

$$Lz_j = Vy_j - Wx_j \qquad (4)$$

$$y_j/x_j = K \qquad (5)$$

where z_j = mole fraction of component j in the leaking liquid

y_j = mole fraction of component j in the vapor

x_j = mole fraction of component j in the liquid after flash

K = equilibrium distribution coefficient

Equation (5) is an equation of state, and K is dependent on system temperature, pressure, and component concentrations. As shown in Table 1, the amount of contaminant

TABLE I
Calculation of Emissions (Q)

1. If the liquid leak rate (L) is known or estimated

   a. for gases in solution

   $$Q = (C - C_o) L \quad (1)$$

   Q = contaminant emission rate (g/s)

   C = contaminant concentration in the process stream (weight fraction)

   C_o = contaminant concentration remaining in the liquid after vaporization (weight fraction)

   L = liquid leak rate, weight basis (g/s)

   b. for hydrocarbon mixtures

   $$Q = yVM \quad (6)$$

   y = mole fraction of the contaminant in the leaking vapor

   V = vapor leak rate, mole basis (g mol/s)

   M = contaminant molecular weight (g/g mol)

2. If the vapor leak rate (E) is known or estimated

   a. for gases in aqueous solution

   $$Q = E \quad (7)$$

   E = vapor leak rate, weight basis (g/s)

   b. for liquid hydrocarbon mixtures

   $$Q = y (M/M_T) E \quad (8)$$

   M_T = vapor mixture molecular weight (g/g mol)

   c. for gas mixtures

   $$Q = CE \quad (9)$$

leaving a pump in the vapor phase when L is known or estimated and V is calculated above, is as follows:

$$Q = yVM \quad (6)$$

where M = molecular weight of the contaminant

The enthalpy balance and Equation 5 makes manual calculation of the mole fraction, y, very cumbersome for real situations. The balance is needed since the heat of vaporization is supplied by the decrease in sensible heat of the leaking material, and hence there is a decrease in the system temperature from the pump temperature to some calculated temperature in the pump seal cavity. For even a simple binary system in which the pumped fluid temperature, pressure, and composition are known, a manual calculation of the amount of contaminant in the vapor requires two major

trial-and-error procedures.[13] Therefore, computer flash calculations are necessary for practically every real situation where multi-component mixtures are common. In many cases pseudo-components must be generated from distillation curves before flash calculations can be started. Again, computer calculations are a necessity. Finally, a large data base can include enough equilibrium data to calculate accurate K values.

If the vapor leak rate is known or estimated, the equations are simplified (Table I). For a gas in solution:

$$Q = E \quad (7)$$

and for gas mixtures:

$$Q = CE \quad (8)$$

TABLE II
Maximum Aqueous Concentrations of Non-Hydrocarbon Contaminants in the Liquid in a Pump Cavity with a Single Mechanical Seal[A]

Contaminant	Aqueous Concentration (Weight %)
Ammonia	15.6
Chlorine	0.78
Hydrogen sulfide	0.65
Carbon monoxide	10.4
Nitric oxide	1.75

[A]Assuming the following conditions:

temperature = 333 K (140°F)
leak rate = 7.6 liters/hour (2 gallons/hour)
worker distance = 2 meters
wind speed = 1 meter/second

For liquid hydrocarbon mixtures:

$$Q = y (M_l M_T)E \qquad (9)$$

where y must be calculated via equations 2 through 5. The emission rate, E, is assumed in the following examples.

Contaminant Evaporation from Non-Operating Equipment

Non-operating equipment, unlike operating equipment previously discussed, is usually at ambient temperature and pressure. Instead of flash vaporization, evaporation is the process that governs the amount of contaminant released to the atmosphere.

Evaporation is a function of vapor pressure and wind speed. Clancey[12] and Sutton[13] have developed an equation that can be used in determining the evaporation rate from a pool of spilled liquid:

$$W = 79.6 \left(\frac{P_T^* M_T}{T}\right) u^{0.78} r^{1.89} \qquad (10)$$

where M_T = material average molecular weight (g/g mol)

   P_T^* = liquid vapor pressure in atmospheres

   T = temperature in Kelvin

   u = wind speed in meters/s

   r = radius of spilled material in meters

   W = evaporation rate in grams/s

The rate of contaminant emission rate, Q, is:

$$Q = y_L W \qquad (11)$$

For a conservative estimate, assume that during maintenance of out-of-service equipment, toxic material is spilled and dispersed to the worker's nose. If the calculated exposure concentration is above the STEL of the material, then flush connections and drain connections to a closed system are recommended to allow the worker to clean the equipment properly before maintenance.

Dispersion of Contaminants from Leaking Equipment

The Gaussian model for predicting downwind concentrations due to dispersion of a gas or vapor reduces to the following equation when only the centerline concentration is estimated:[14]

$$x = \frac{Q (1000)}{2\pi \sigma_y \sigma_z u} \qquad (12)$$

The following dispersion coefficients are applicable to Equation 12:

$$\sigma_y = 0.195 \, x^{0.90} \qquad (13)$$

$$\sigma_z = 0.112 \, x^{0.91} \qquad (14)$$

After substitution, the final equation is:

$$x = \frac{(1000) Q}{(0.136) x^{1.81} u} \qquad (15)$$

where   X = concentration at worker in milligrams cubic meter

   Q = contaminant emission rate in grams/s

   x = distance between the emission source and the worker in meters

   u = wind speed in meters/s

This model is suggested as a tool for estimating worker exposure concentrations due to leaking equipment. The dispersion coefficients σ_y and σ_z are approximations to Pasquill-Gifford "C" stability. The equation is based on the receptor (the worker's nose) located directly downwind of a source, and close enough to the source that ground reflection is not important. These considerations result in an equation that is a conservative estimating tool. The equation is time-averaged on a 10-minute basis.

Unpublished data collected at an Exxon facility suggest Equation 15 predicts downwind concentrations, at wind speeds of 0.5-3 meters/second and distances up to 3 meters.
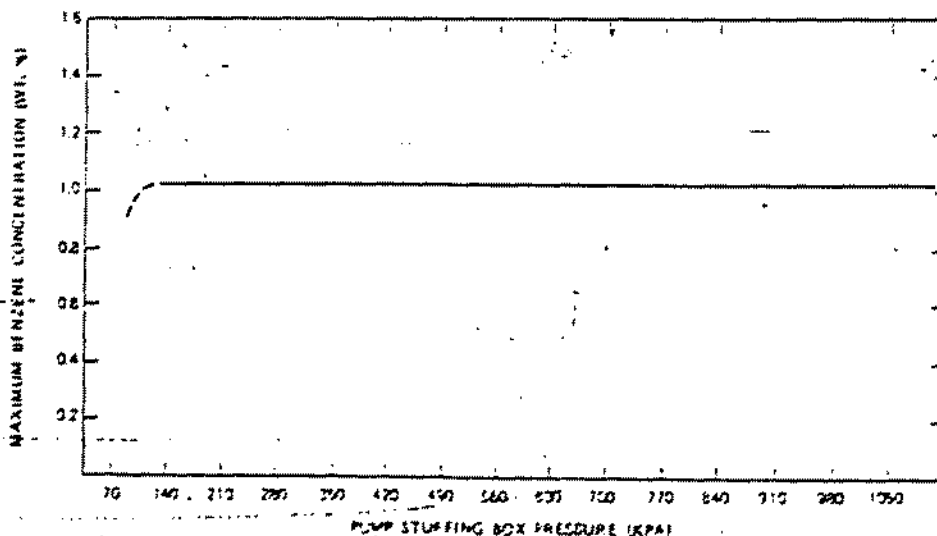

Figure 4 — The effect of pump stuffing box pressure on the maximum concentration of benzene in tetralin in a centrifugal pump

within the 95 percent confidence limits of the data. Further model confirmation is now in progress at an Exxon facility.

Example Calculation 1 — Hydrogen Sulfide Leaking from a Pump Seal

Assume a pressurized water stream contains 1.5 weight percent H_2S as the only major contaminant. The aqueous stream is approximately pH = 7 and will hold 0.2 weight percent H_2S in solution at atmospheric pressure.

$$C = 0.015 \text{ weight fraction}$$
$$C_o = 0.002 \text{ weight fraction}$$
$$L' = 7.6 \text{ liters} \cdot \text{hour}$$
$$= 2.1 \text{ g/s}$$

$$Q = (C - C_o) L' \qquad (1)$$
$$= (0.015 - 0.002) \, 2.1$$
$$= 0.027 \text{ g/s}$$

To estimate the potential concentration at the workers nose, a wind speed and distance must be assumed. For conservative purposes, choose u = 1 m/s. For worker repairing a pump located near the leaking pump, a 2 meter distance is a good approximation for x:

$$x = \frac{(1000) \, Q}{(0.136) \, x^{1.91} \, u} \qquad (15)$$

$$x = \frac{(1000)(0.027)}{(0.136) \, 2^{1.91} \, (1)}$$

$$x = 55.2 \text{ mg/m}^3$$

Since 55.2 mg/m³ is above the STEL[15] for hydrogen sulfide, which is 21 mg/m³, the pump seal should be upgraded (for

example, to a double mechanical seal) to prevent seal leaks from over-exposing workers to H_2S. Table II shows several maximum aqueous concentrations for non-hydrocarbon contaminants that were calculated at the same wind speeds and distances assumed above.

Example Calculation 2 — Liquid Hydrocarbon Mixture Leaking from a Pump Seal

Assume 2 weight percent benzene in a stream of tetralin (a representative higher molecular weight aromatic compound) is pumped at 447 kPa (65 psia) and 477 K (400°F). (Normally, hydrocarbon mixtures are complex with several boiling range fractions that are not readily identifiable compounds. Computer programs are available to consolidate the properties of the hydrocarbon mixture such that a pseudo-component, not multi-fraction, system can be assumed.) As noted above, a manual or computer calculation is available to estimate the rate of moles of vapor leaving a leaking pump, V, and the fraction of benzene in that vapor, y, if the hydrocarbon liquid leak rate is known or estimated. If the liquid leak rate is unknown, and instead E, the vapor leak rate on a weight basis, is known or estimated, Equations 2 though 5 still must be used to determine y for Equation 8.

For this example, choose E = 0.341 g/s (2.7 pounds/hour). Equations 2 through 5 via computer program give y = 0.248 mole fraction:

$$Q = y \, \frac{M}{M_T} \, E \qquad (9)$$

where $M = 78$ g/g mol for benzene

$M_T = 119$ g/g mol for benzene/tetralin mixture in vapor

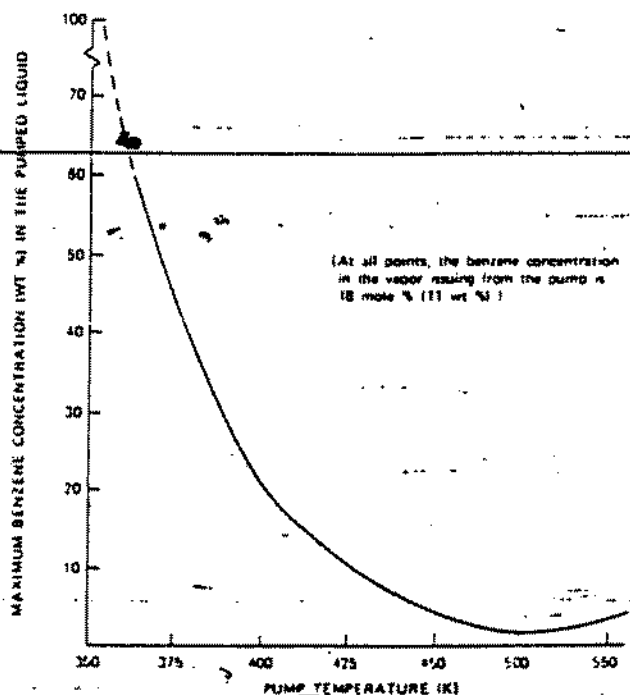$$Q = (0.248) \left(\frac{78}{130}\right) (0.341) = 0.051 \text{ g/s}$$

Figure 5 — The effect of temperature on the maximum concentration of benzene in tetralin in a centrifugal pump.
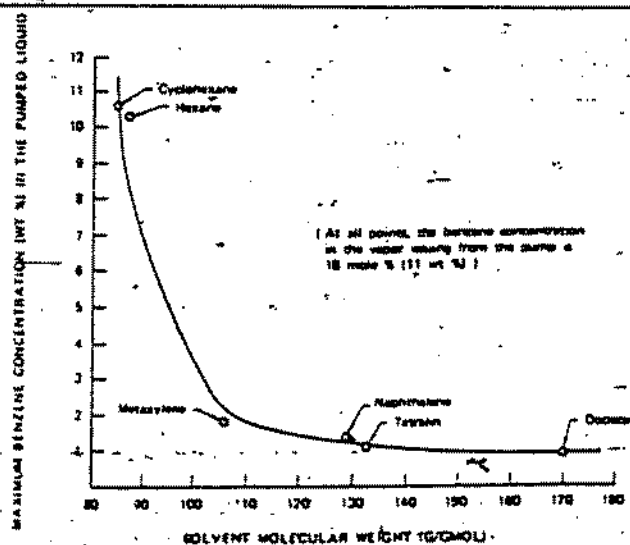

Figure 6 — The effect of solvent type on maximum concentration of benzene in a centrifugal pump.
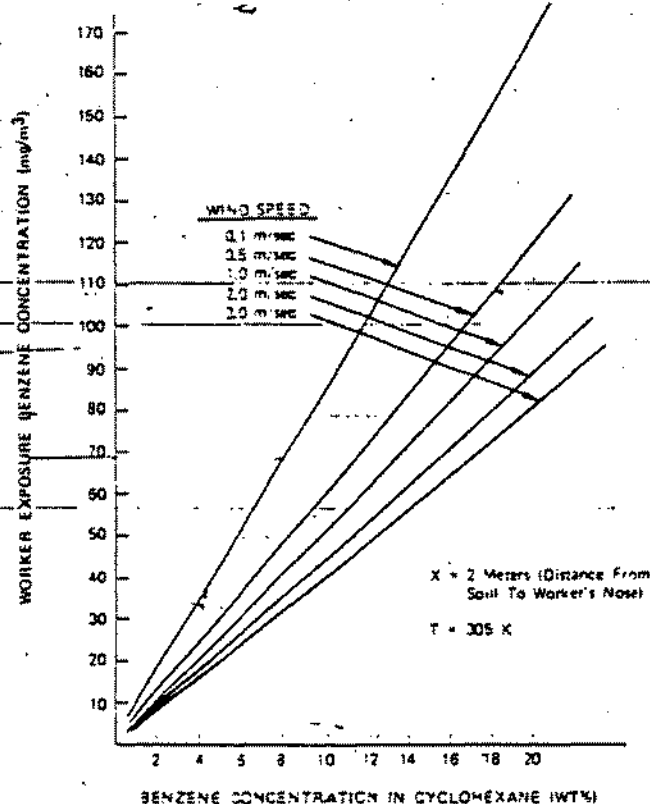
Figure 7 — The effect of wind speed and evaporating liquid benzene concentration on the worker exposure concentration of benzene.

Similar to the above example, choose u = 1 meter/s, and x = 2 meters:

$$\chi = \frac{(1000)\,Q}{(0.136)\,x^{1.14}\,u} \qquad (15)$$

$$\chi = \frac{(1000 \times 0.051)}{(0.136)\,2^{1.14}\,(1)}$$

$$\chi = 104 \text{ mg/m}^3$$

Since 104 mg/m³ is above the STEL for benzene, which is 75 mg/m³, the single mechanical pump seal should be upgraded to a multiple seal. Figures 4-6 show the effect of

pumping pressure, temperature, and solvent on the maximum hydrocarbon mixture concentration of benzene.

Example Calculation 3 — Gas Mixture Leaking from a Valve

Assume a 4 weight percent ammonia in nitrogen stream is leaking from a valve, and the valve leak increases to 0.038 g/s (0.3 pounds per hour) before the valve is shut down for repair. The amount of ammonia leaking from the valve under the worst conditions is:

$$Q = CE \qquad (9)$$

$$Q = 0.04(0.038 \text{ g/s})$$

$$= 0.0015 \text{ g/s}$$

If u = 1 meter/s, and x = 2 meters:

$$\chi = \frac{1000\,(0.0015)}{(0.36)\,2^{1.14}\,(1)}$$

$$= 3.07 \text{ mg/m}^3$$

Since the STEL for ammonia is 27 mg/m³, the packing in this valve does not require upgrading.

Example Calculation 4 — Hydrocarbon Mixture Evaporation from Out-of-Service Equipment

Assume a pump containing 1 weight percent benzene in 99 weight percent cyclohexane is withdrawn from service for maintenance. The temperature of the pump is 305 K (90° F) and the pump contents (200 milliliters) are spilled on to the pump pad:

$$W = 79.6 \left(\frac{P_T M_T}{T}\right) u^{0.78} r^{1.89} \qquad (10)$$

For 1 weight percent benzene, the mole fractions are:

$$X_{benzene} = 0.011$$

$$X_{cyclohexane} = 1 - X_{benzene} = 0.989$$

The material average molecular weight, M_T, the total vapor pressure P_T, and T are:

$$M_T = (0.011)(78 \text{ g/g mol}) - 0.989(84 \text{ g/g mol}) = 84 \text{ g/g mol}$$

at 305 K, $P^{\circ}_{benzene} = 17.2$ kPa, $P^{\circ}_{cyclohexane} = 18.2$ kPa

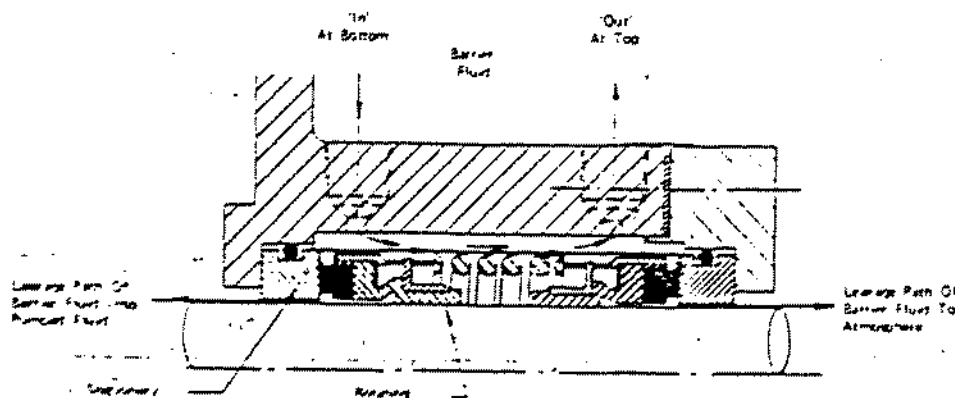$$P_T = 0.011(17.2) - 0.989(18.2) = 18.2 \text{ kPa } (0.18 \text{ atm})$$

Figure 8 — Centrifugal pump double mechanical seal

If the spill depth is approximately 1 millimeter:

$$r = \sqrt{\frac{200\ cm^2}{\pi(0.1\ cm)}}\ (0.01\ \frac{meter}{centimeter}) = 0.252\ meter$$

Assume $u = 1$ meter/s. Therefore:

$$W = 79.6\ \frac{(0.18)(84)}{305}\ (1)^{0.78}\ (0.25)^{1.89}$$

$$= 0.287\ g/s$$

and $Y_{benzene} = \frac{X_B\ P_B^0}{P_T} = \frac{(0.01)(0.17)}{(0.18)} = 0.01$

$$Y_{cyclohexane} = \frac{X_{CH}\ P_{CH}^0}{P_T} = \frac{0.989\ (0.18)}{0.18} = 0.99$$

$$Q_{benzene} = (0.01)(0.287) = 0.00287\ g/s$$

$$Q_{cyclohexane} = (0.99)(0.287) = 0.284\ g/s$$

Using Equation 13:

$$X = \frac{(1000)\ Q}{(0.136)\ x^{1.77}\ u} \qquad (13)$$

If $x = 2$ meters:

$$X_{benzene} = \frac{(1000)(0.00287)}{(0.136)\ 2^{1.77}\ (1)} = 5.88\ mg/m^3$$

$$X_{cyclohexane} = \frac{(1000)(0.284)}{(0.136)\ 2^{1.77}\ (1)} = 582\ mg/m^3$$

Since the STEL limits for benzene and cyclohexane are 75 mg/m³ and 1300 mg/m³, respectively, the pump does not require closed drains and flushing connections on this basis to thoroughly purge and clean the pump prior to removing the pump from service. However, since a machinist may spend several hours working in the pump vicinity at a distance less than 2 meters from the pump and since benzene exposure can cause severe chronic effects, flushing connections and drains should be installed.

Figure 7 shows the effect of wind speed and benzene concentration on the worker exposure concentration.

Equipment Improvement

If the industrial hygienist estimates in the design stage that over-exposure is possible from an equipment source, sufficient time is available to recommend engineering controls to protect workers. For pumps, the engineering controls may be auxiliary packing (Figure 2) or a dual seal pump, i.e., tandem seal or double mechanical seal (Figure 8). As noted previously, concern for maintenance workers around equipment may lead to permanent drain and flushing connections. Reference 16 has several examples of engineering controls in process equipment.

Conclusion

A rough calculation method exists to estimate the exposure of workers to material leaking from process equipment. In all but the simplest system, a computer calculation is required to estimate the equilibrium vapor concentrations of flashing liquid contaminants. An evaporation model and a dispersion model, both of which have a minimum of confirming data, are available for estimating exposures. However, the complete system, i.e., from a leaking equipment source to a worker's nose, requires more field data to insure confidence in the accuracy of the estimates.

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APPENDIX B

Name of Facility:	Northwest Foam Products, Inc.		
AIRS/Permit #:	083-00063		
Permit Issue Date:			

Source/Emissions Unit Name (25 spcs) (Please Use Name As Indicated In Permit)	SCC # (8 digit #)	Air Program (/ P/ S/)
MANUFACTURING Building 1, Boilers #1-4 Common Stack	10200603	Tier 2 S I P